Stable Carbonium Ions. LXII.[1a] Halonium Ion Formation *via* Neighboring Halogen Participation: Ethylenehalonium, Propylenehalonium, and 1,2-Dimethylethylenehalonium Ions

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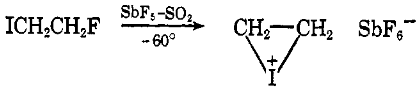
Abstract: Bridged halonium ions were observed to arise on ionization of 1,2-dihaloethanes, 1,2-dihalopropanes, and 2,3-dihalobutanes when the participating atom is iodine or bromine. Starting from *erythro*- or *threo*-2-bromo-3-fluorobutane, the same mixture of *cis*- and *trans*-dimethylethylenebromonium ions was obtained, but from the corresponding iodides, stereospecific formation of the *trans*- and *cis*-1,2-dimethylethyleneiodonium ions, respectively, was observed. These latter ions were stereospecifically solvolyzed in methanol to the reported methyl ether.

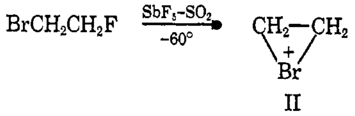
We have recently reported nmr evidence for the existence of bridged tetramethylethylene-, trimethylethylene-, and 1,1-dimethylethylenehalonium ions.[2a,b] We have now completed the investigation of the series of methyl-substituted ethylenehalonium ions, and wish to report the observation of ethylene-, propylene-, and 1,2-dimethylethylenehalonium ions as well as to summarize our evidence for halonium ion formation.

Results and Discussion

Ethylenehalonium Ions. 1-Iodo-2-fluoroethane readily ionizes in antimony pentafluoride–sulfur dioxide with loss of fluoride ion to give the ethyleneiodonium ion I (Figure 1). This conclusion is based on: (1) a sharp singlet in the pmr spectrum indicating loss of fluoride and the production of equivalent methylene groups; (2) substantial downfield shifts of the methylene protons, and (3) isolation of 1-methoxy-2-iodoethane on solvolysis of ion I in methanol.



Similar treatment of 1-bromo-2-fluoroethane resulted in formation of the ethylenebromonium ion II (Figure 2). The nmr spectrum of II consisted of a somewhat broadened singlet (width at half-height of 2.8 Hz compared to 1.8 Hz for ethyleneiodonium ion, both at −60°). Ion II also meets all the requirements for the assigned structure as listed above for the ethyleneiodonium ion I. Cooling the solution of the ethyleneiodonium and bromonium ions to −80° resulted in broadening of the spectral lines with the bromonium ion broadening considerably more than the iodonium ion. This difference in behavior is probably related to the amount of quadrupole coupling in the two species.[3]



II

Raising the temperature of the bromonium ion to −30° resulted in a sharp singlet absorption. At higher temperature decomposition to protonated acetaldehyde begins to take place.

Treatment of 1,2-dichloroethane with antimony pentafluoride in sulfur dioxide results in the formation of several species depending on the concentration of antimony pentafluoride and the temperature. A singlet appears at −3.96 ppm immediately on mixing at −78° which nearly disappears if a large excess of antimony pentafluoride is used. We believe this to be un-ionized and uncomplexed 1,2-dichloroethane. When this singlet disappears it is replaced by a pair of triplets at −4.44 and −5.66 ppm (several smaller absorptions are also beginning to appear). These absorptions may be due to the complex IIIa. If the solution is now warmed to about −10° for 5 min, the major species observed is protonated acetaldehyde[4a] with varying amounts of unknown species. When 1-chloro-2-fluoroethane is treated in the same way, a pair of AA′-XX′-type absorptions (triplets with a complex central peak) appear at −4.52 and −6.53 ppm indicating complex IIIb. Heating this solution briefly again results in the formation of protonated acetaldehyde and an unknown species in nearly equal amounts. In complex IIIb, the lack of fluorine coupling indicates a rapid exchange of fluorine, but since two separate

$SbF_5 \leftarrow ClCH_2CH_2Cl$ IIIa

$SbF_5 \leftarrow FCH_2CH_2Cl$ IIIb

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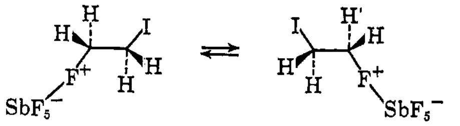
[1] (a) Part LXI: G. A. Olah and T. Kiovsky, *J. Am. Chem. Soc.*, **90,** 2583 (1968). (b) National Science Foundation Undergraduate Research Participant, Summer 1967.

[2] (a) G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, **89,** 4744 (1967); (b) G. A. Olah and J. M. Bollinger, *ibid.*, **90,** 947 (1968).

[3] The halogens all have quadrupole moments increasing in absolute magnitude from chlorine to iodine. The fact that only bromonium ion species are broadened may be related to the carbon–bromine bond length.

[4] (a) G. A. Olah, D. H. O'Brien, and M. Calin, *J. Am. Chem. Soc.*, **89,** 3582 (1967). (b) G. A. Olah and M. B. Comisarow, to be published. (c) A referee has pointed out that the average of the chemical shifts for the two methylene groups of IIIb (5.5 ppm) is in the same region (5.5–5.8 ppm) observed for the equivalent methylene groups of the ethyleneiodonium and -bromonium ions. He further points out that our data are then compatible with a rapid equilibration as shown. We believe that the small geminal coupling constant apparently required for the methylethyleneiodonium ion is more consistent with a hybridization approaching sp². We hope to obtain a direct measure of the geminal coupling constants in the ethyleneiodonium and -bromonium ions by analysis of the C¹³ satellite spectra.



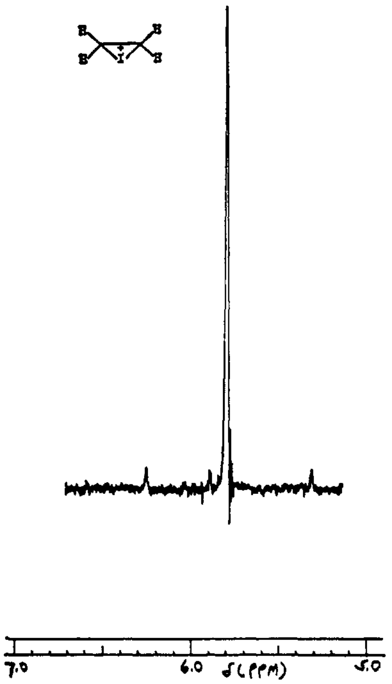


Figure 1.

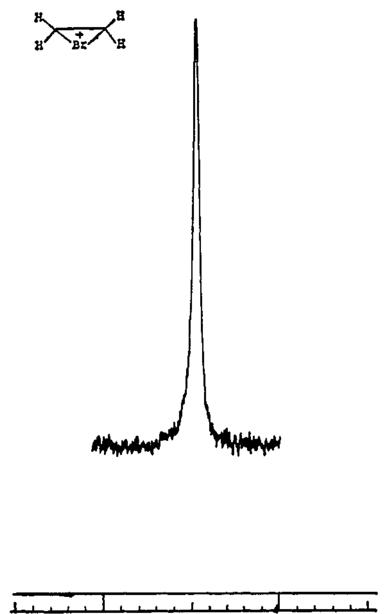


Figure 2.

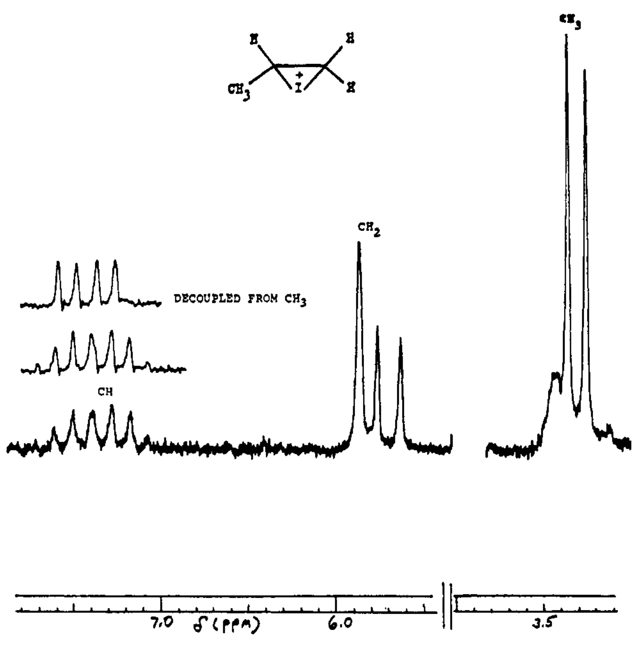


Figure 3.

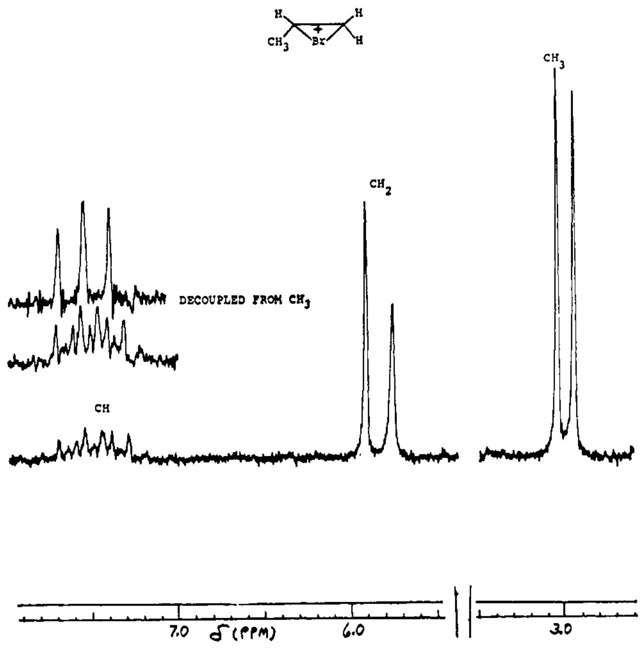


Figure 4.

methylene absorptions are observed, there is not rapid chlorine migration. Similar disappearance of fluorine coupling is observed for methyl and ethyl fluorides in solution in antimony pentafluoride–sulfur dioxide without sufficient downfield shift to indicate ionization of these species.[4b,c]

When 1,1-dichloroethane is dissolved in antimony pentafluoride–sulfur dioxide with warming to −40°, protonated acetaldehyde is immediately formed together with considerable amounts of 1,1-difluoroethane. The reactions described above leading to protonated acetaldehyde have precedent in other strong acids[4a,5] and a possible mechanism is detailed below.[6] Protons are generally present as an impurity in the antimony pentafluoride–sulfur dioxide solution. This reaction has also been observed in antimony pentafluoride–fluorosulfonic acid–sulfur dioxide solution.[4a] Similar results were obtained with 1,1-dibromoethane. These results are summarized in Table I.

Propylenehalonium Ions. We next examined ions produced from 1,2-dihalopropanes. 2-Fluoro-1-iodo-

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(5) Geminal dichlorides and difluorides can be hydrolyzed to ketones and aldehydes in aqueous sulfuric acid; *cf.* H. Hart, J. A. Hartlage, R. W. Fish, and R. Rafos, *J. Org. Chem.*, **31**, 2244 (1966). Similarly, perhalomethyl groups are hydrolyzed to acids under similar conditions; *cf.* N. C. Deno, N. Friedman, and J. Mockus, *J. Am. Chem. Soc.*, **86**, 5676 (1964), and R. J. Gillespie and E. A. Robinson, *ibid.*, **86**, 5676 (1964).

(6) We will report in a forthcoming paper in detail an investigation of the mechanism of reactions of this type.

Table I. Nmr Spectral Data of Ethylenehalonium Ions, Precursors, and Methanolysis Products[g]

Compound	δ, ppm Compd in CCl_4[a,d]	Compd in SbF_5–SO_2[a,e]	Methanolysis prodt in CCl_4[a,b,d]	ϕ, ppm in CCl_4[a,f]	Δδ
$ClCH_2CH_2Cl$	3.66 (s)	3.96 (s)[c]			
		4.44 (t)			
		5.66 (t)			
$ClCH_2CH_2F$	3.67 (d) J_{H-F} = 23.0	4.52 (t)			
		(AA'XX')		+209.9 (t) J_{H-F} = 46	
	(t) J_{H-H} = 6.0	6.53 (t)			
	4.58 (d) J_{H-F} = 46.0			(t) J_{H-F} = 23	
	(t) J_{H-H} = 6.0				
$BrCH_2CH_2F$	3.49 (d) J_{H-F} = 18.5	5.53 (s, broad)	3.25–3.80 (m) (51%)	+211.1 (t) J_{H-F} = 46	2.04
	(t) J_{H-H} = 6.0		3.37 (s)	(t) J_{H-F} = 18.5	0.92
	4.61 (d) J_{H-F} = 46.0				
	(t) J_{H-H} = 6.0				
ICH_2CH_2F	3.37 (d) J_{H-F} = 19.0	5.77 (s)	3.3 (m)	+209.4 (t) J_{H-F} = 47	2.40
	(t) J_{H-H} = 6.0		(58%)	(t) J_{H-F} = 19	1.20
	4.57 (d) J_{H-F} = 47.0		3.63 (s)		
	(t) J_{H-H} = 6.0		4.2 (m)		
CH_3CHCl_2	2.03 (d) J_{H-H} = 6.0	*c*			
	5.86 (q) J_{H-H} = 6.0				
CH_3CHBr_2	2.47 (d) J_{H-H} = 6.0	*c*			
	5.86 (a) J_{H-H} = 6.0				

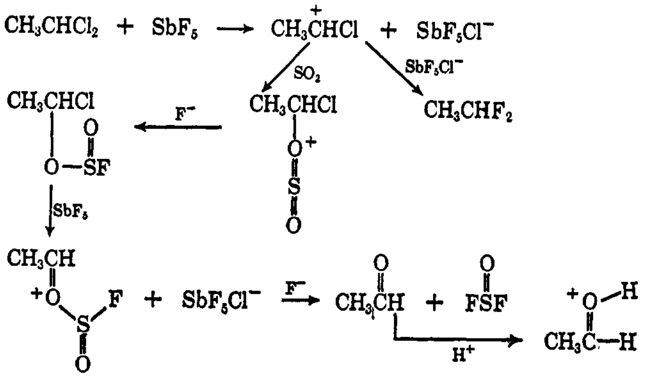
[a] Abbreviations used are: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. [b] Figures in parentheses are isolated yields. [c] See text for structural assignment. [d] Internal TMS. [e] External TMS. [f] Internal $CFCl_3$. [g] *J* values in hertz.

Table II. Nmr Spectral Data for Propylenehalonium Ions, Precursors, and Methanolysis Products[g]

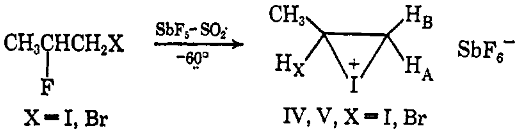
Compound	δ, ppm Compd in CCl_4[a,d]	Compd in SbF_5–SO_2[a,e]	Methanolysis product in CCl_4[a,b,d]	ϕ, ppm in CCl_4[a,f]	Δδ
$ClCH_2CHClCH_3$	1.70 (d) J_{H-H} = 6.5	Polymer			
	3.8 4.3 $ABCX_3$				
$BrCH_2CHFCH_3$	1.50 (d) J_{H-F} = 23	2.98 (d) J_{H-H} = 6.0	1.25 (m)	+170 (d) J_{H-F} = 47	1.48
	J_{H-F} = 6.0	5.86 (d)	3.1–3.5 (m) (60%)	(q) J_{H-F} = 23	2.46
	3.40 (d) J_{H-F} = 1.7	7.48 (m)	3.32 (s)	(t) J_{H-F} = 1.7	2.71
	(d) J_{H-H} = 5.0				
	(sextet) J_{H-H} = 6.0				
	4.77 (d) J_{H-F} = 47				
ICH_2CHFCH_3	1.46 (d) J_{H-H} = 6.0	3.32 (d) J_{H-H} = 6.0	1.23 (m)	+163 (d) J_{H-F} = 48	1.86
	(d) J_{H-F} = 22.5	5.77 (t)	3.0–3.4 (m) (63%)	(q) J_{H-F} = 22.5	2.53
	3.24 (d) J_{H-H} = 6.0	7.33 (m)	3.30 (s)	(t) J_{H-F} = 1.8	2.71
	(d) J_{H-F} = 1.8				
	(sextet) J_{H-H} = 6.0				
	4.62 (d) J_{H-F} = 48				
$BrCH_2CHBrCH_3$	1.82 (d) J_{H-H} = 6.5	2.98 (d) J_{H-H} = 6.0	1.25 (m)		1.16
	3.7 4.3 $ABCX_3$	5.86 (d)	3.1–3.5 (m) (68%)[c]		2.16
		7.48 (m)	3.32 (s)		3.18

[a] Abbreviations used are: s = singlet, t = triplet, q = quartet, d = doublet, m = multiplet. [b] Figures in parentheses are isolated yields. [c] See discussion in text. [d] Internal TMS. [e] External TMS. [f] Internal $CFCl_3$. [g] *J* values in hertz.

propane and 2-fluoro-1-bromopropane form the bridged propyleneiodonium ion IV (Figure 3) and the propylenebromonium ion V, respectively (Figure 4).



The spectra of the precursors to these ions are complicated since they are $ABCX_3$ systems. We did not analyze these spectra completely and the shift values reported in Table II are approximate for the ABC protons.



The spectra observed for these ions are of the $ABKX_3$ type and an analysis was attempted. Unfortunately, the spectra of ions IV and V were deceptively simple and exact solutions could not be calculated. Spectra were obtained at 100 MHz in addition to the 60-MHz spectra. For the propyleneiodonium ion, it was pos-

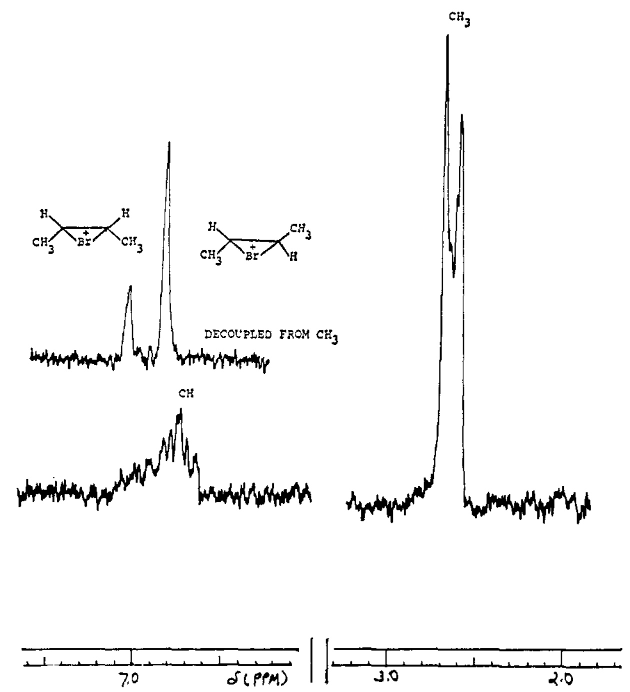


Figure 5.

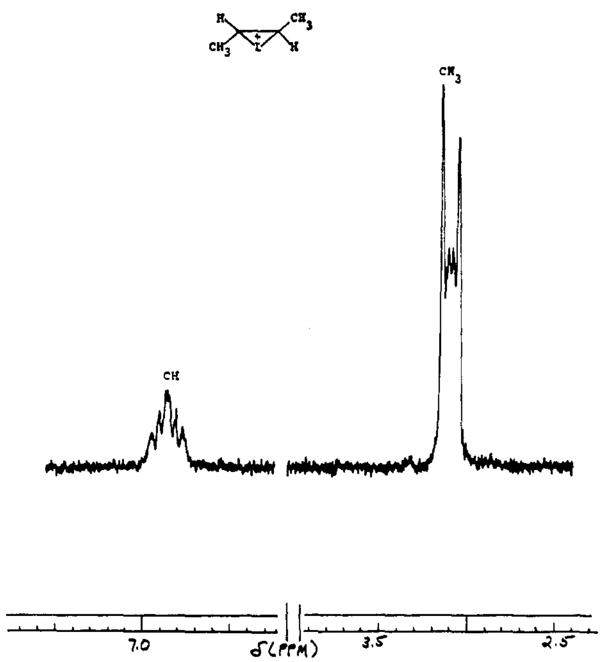
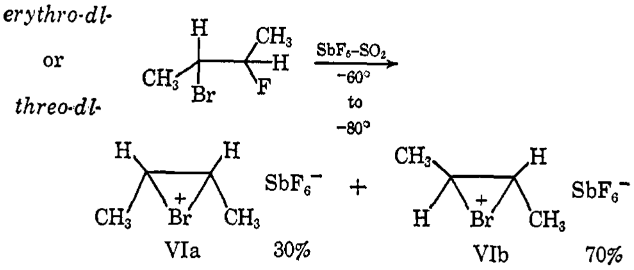


Figure 6.

sible to calculate values of J_{AX} and J_{BX} for assumed values of J_{AB}. Thus as J_{AB} varies from 0 to 12 Hz, J_{AX} varies from 5.7 to 5.1 and J_{BX} varies from 13.9 to 14.5 ($J_{AX} + J_{BX} = 19.6$ Hz). The assignment of chemical shift for the A and B protons was made by analogy with the 1,2-dimethylethyleneiodonium ions to be discussed subsequently. We conclude that the most probable value for J_{AB} is 0 Hz. For the propylenebromonium ion, the only conclusion which can be made is that $J_{AX} + J_{BX} = 18.0$ Hz.[7,8]

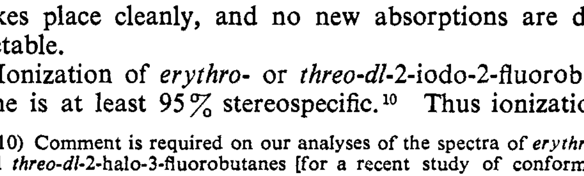
We were unable to prepare the methylethylenechloronium ion from 1,2-dichloropropane. No resonance signals of any defined ion were observed apparently because of polymerization. Table II summarizes the nmr data.

1,2-Dimethylethylenehalonium Ions. Bridged halonium ions were formed from *meso*- and *dl*-dibromobutanes, and from *erythro*- and *threo*-*dl*-2-bromo-3-fluorobutanes. Starting from either configurational isomer in the brominated materials resulted in a mixture of two ions presumably the *cis*- and *trans*-halonium ions VIa and VIb (Figure 5). The spectra are complicated (they are $A'AX_3X_3'$ systems[9]) but double irradiation resulted in the formation of singlets (somewhat broadened) which revealed the presence of the two singlets in the methine region separated by 12 Hz. Regardless of the care used in preparation of these ions, the same mixture was obtained.



Our starting materials were better than 95% pure. It is not certain in this case whether equilibration takes place during ionization or whether ionization is stereospecific (as required by neighboring group participation) and equilibration takes place during the extremely long lifetime of the bridged ion.

Warming the isomeric 2,3-dimethylethylenebromonium ions to −40° for about 5 min causes isomerization to take place to give the previously reported 1,1-dimethylethylenehalonium ion[2b] (VIc). The isomerization takes place cleanly, and no new absorptions are detectable.



Ionization of *erythro*- or *threo*-*dl*-2-iodo-2-fluorobutane is at least 95% stereospecific.[10] Thus ionization

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(7) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, 40, 875 (1962), and references therein.

(8) R. J. Abraham and H. J. Bernstein, *ibid.*, 39, 216 (1961).

(9) R. K. Harris, *ibid.*, 42, 2275 (1964).

(10) Comment is required on our analyses of the spectra of *erythro*- and *threo*-*dl*-2-halo-3-fluorobutanes [for a recent study of conformational preferences in diastereoisomers, see C. A. Kingsbury and D. C. Best, *J. Org. Chem.*, 32, 6 (1967)]. We have used a first-order analysis to obtain the observed chemical shifts and coupling constants. This treatment is adequate when the halogen is chlorine or bromine, but breaks down for the iodine-containing molecules. This failure of the first-order treatment is obvious from the appearance of new absorptions in the proton spectra. We are currently trying to analyze these spectra exactly.

Similarly, we used a first-order analysis on the 1-halo-2-fluoroethane compounds which are actually much more complicated spectra [R. J. Abrahamson, L. Carelli, and K. G. R. Pachler, *Mol. Phys.*, 11, 471 (1966), have reported an nmr study of some 1-halofluoroethane derivatives.]

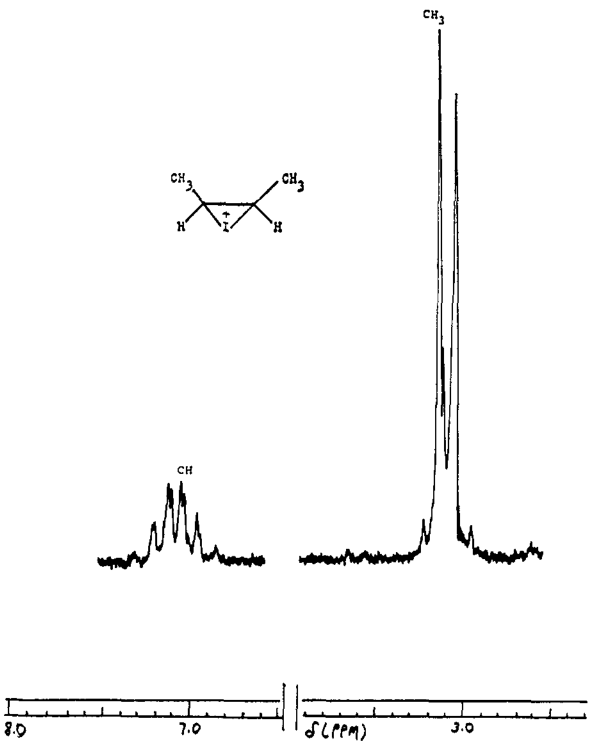
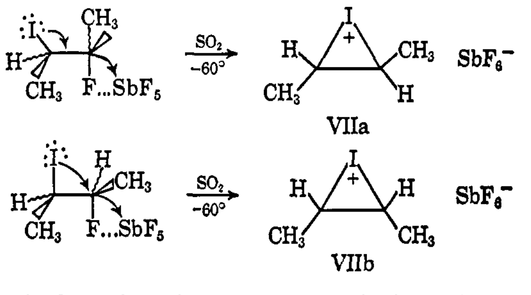
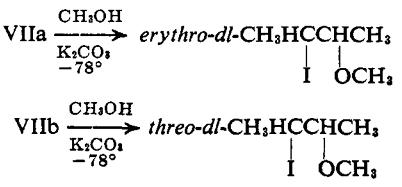


Figure 7.

of *erythro-dl*-2-iodo-2-fluorobutane produces an ion to which we have assigned the *trans* configuration VIIa (Figure 6), and ionization of *threo-dl*-2-iodo-2-fluorobutane produced a different ion to which we have assigned the *cis* configuration VIIb (Figure 7). No detectable (by nmr) intercontamination of the ions was observed. These structural assignments of the ions were based largely on expectation. Support for these assignments was found in the methanolysis of the ions in the presence of solid potassium carbonate which produced *erythro-dl*-2-iodo-3-methoxybutane and *threo-dl*-2-iodo-3-methoxybutane, respectively, without detectable (by nmr) contamination with the other stereoisomer (by comparison with the authentic materials). However, vpc analysis on a capillary column indicated the presence of approximately 3–4% of the other isomers. This most likely represents either slight leakage in the quenching process or nondetectable isomerization in the ionization process since our starting materials were better than 98% pure by vpc analysis.





$$\text{VIIa} \xrightarrow[\substack{K_2CO_3\\ -78^\circ}]{CH_3OH} \textit{erythro-dl-}CH_3\underset{\text{I}}{\text{CH}}\underset{OCH_3}{\text{CH}}CH_3$$

$$\text{VIIb} \xrightarrow[\substack{K_2CO_3\\ -78^\circ}]{CH_3OH} \textit{threo-dl-}CH_3\underset{\text{I}}{\text{CH}}\underset{OCH_3}{\text{CH}}CH_3$$

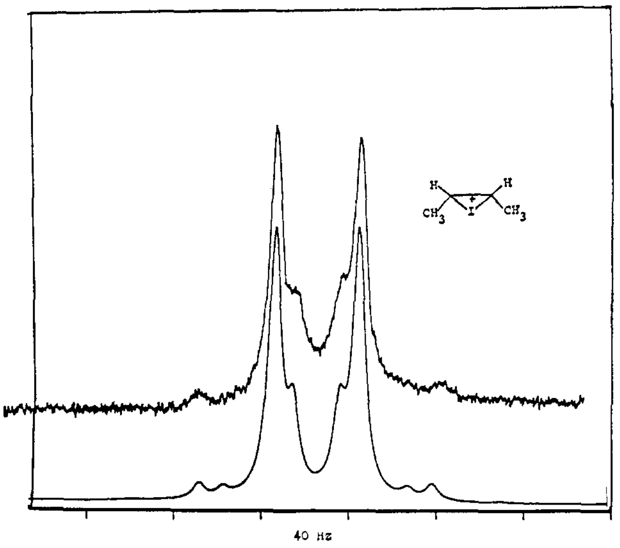


Figure 8. Observed (upper line) and computer-simulated (lower line) pmr spectra.

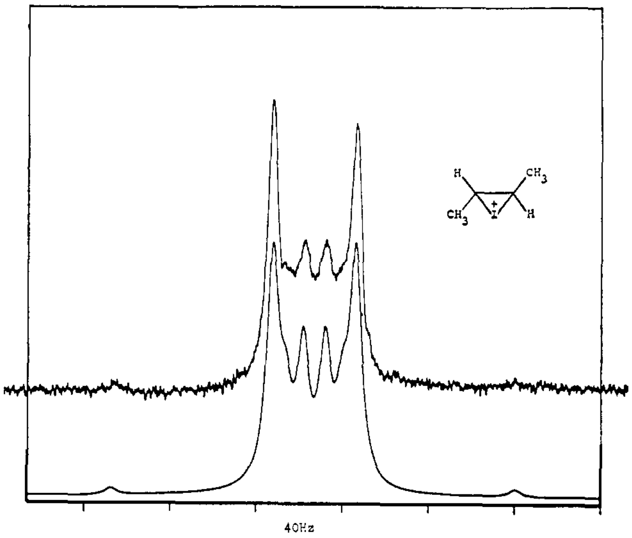


Figure 9. Observed (upper line) and computer-simulated (lower line) pmr spectra.

The methine absorptions of VIIa and VIIb are separated by nearly 0.3 ppm, but the methyl resonances overlap. Precise measurements were made on mixtures of the ions to guard against any uncertainties arising from instrumental or concentration effects.

These chemical shift differences for methine protons provide support for the structural assignments. Thus one would conclude that the methine protons in VIIa should be most effectively shielded by the neighboring carbon–carbon bonds, whereas in VIIb the methine protons are relatively open and should appear at low field.[11] These same considerations were applied to shift assignments in the 1,2-dimethylethylenebromonium ions and the propyleneiodonium ion.

Using the method of Anet,[12] we were able to analyze the nmr spectra for the *cis*- and *trans*-1,2-dimethylethyleneiodonium ions (as $X_3AA'X_3'$ systems). The values giving the best fit were J_{AX} = 6.4 Hz, $J_{AX'}$ = −0.7

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[11] S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Am. Chem. Soc.*, 87, 5247 (1965).

[12] F. A. L. Anet, *ibid.*, 84, 747 (1962).

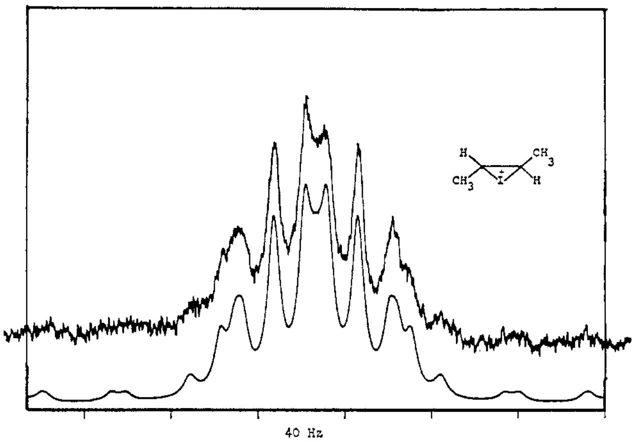


Figure 10. Observed (upper line) and computer-simulated (lower line) pmr spectra.

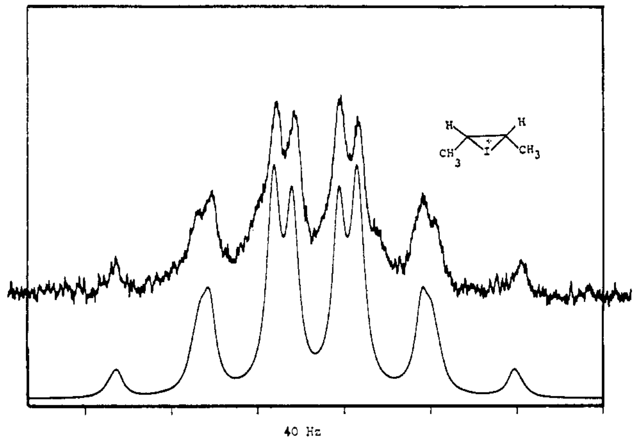
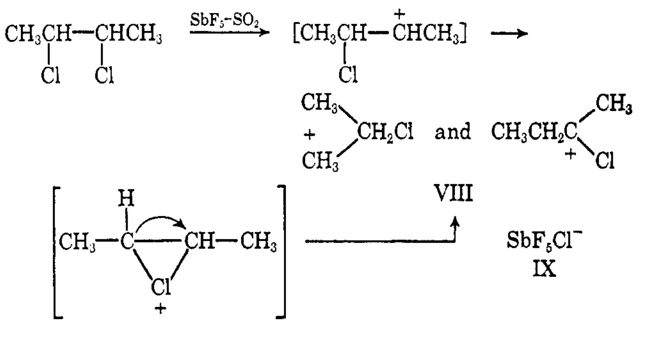


Figure 11. Observed (upper line) and computer-simulated (lower line) pmr spectra.

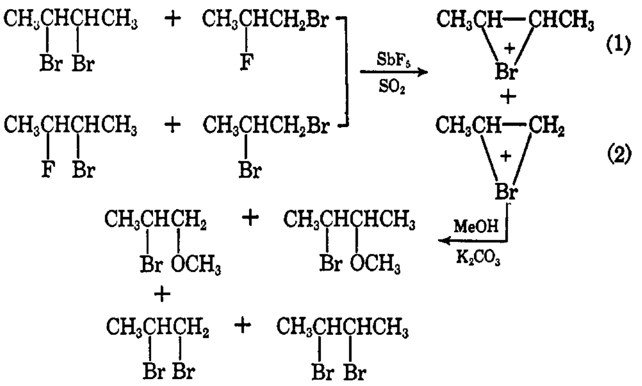
Hz, and $J_{AA'}$ = 6.5 Hz for the *cis* ion and J_{AX} = 6.2 Hz, $J_{AX'}$ = −0.4 Hz, and $J_{AA'}$ = 13.3 Hz for the *trans* ion ($J_{XX'}$ assumed to be 0). The spectra were then simulated by computer (Figures 8–11).

The isomeric stability of these ions is somewhat surprising. No corresponding rearrangement of the 2,3-dimethylethyleneiodonium ions to 1,1-dimethylethyleneiodonium ion or interconversion of the stereoisomers could be detected after 10 min at −15°, although prolonged storage around this temperature results in some conversion of each isomer to the other. Qualitatively, it appears that the *cis* → *trans* isomerization is considerably faster than the *trans* → *cis* as one would expect, although these differences could be caused (or considerably affected) by concentration variations.

Ionization of *erythro*- or *threo*-2-fluoro-3-chlorobutane or *meso*- or *dl*-2,3-dichlorobutane results in immediate rearrangement to a mixture of ions VIII and IX, 40 and 60%, respectively, as reported by us previously.[2b] This occurs cleanly with no side products detectable. Whether an intermediate chloronium ion is involved in the rearrangement cannot be decided.

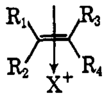


All of the halonium ions reported here have been solvolyzed in methanol in the presence of solid potassium carbonate. In all cases, except that of the mixture of the chloro-*t*-butyl cation and the methylethylchlorocarbonium ion, quenching gave good yields of the expected ethers. However, we were surprised to find that solutions of bromonium ions, prepared by ionization of dibromides in antimony pentafluoride–sulfur dioxide solutions, gave considerable quantities of dibromide on quenching in methanol–potassium carbonate suspension at −78°. We have performed a series of experiments which conclusively demonstrate that the dibromide obtained in quenching experiments arises from "external bromide" and not as a result of incomplete ionization or ion-pair phenomena. The first experiment consisted of a crossover experiment illustrated below.



The appearance of the crossover products $CH_3C(Br)HCH_2Br$ in eq 1 and $CH_3C(Br)HC(Br)HCH_3$ in eq 2 shows that bromide comes from an external source, and not simply from a failure to effect a complete ionization. Conclusive proof was obtained from quenching ethylenebromonium ion prepared from 1-bromo-2-fluoroethane in methanol in which a potassium bromide in antimony pentafluoride–sulfur dioxide solution had been previously quenched. In this case 1,2-dibromoethane constituted nearly 50% of the organic product. We conclude that the ion SbF_5Br^- competes quite well with methanol for the halonium ion, and since nearly all the charge is concentrated on bromine, this is the most nucleophilic end of the ion.

In our previous papers[2a,b] we presented evidence for the cyclic nature of tetramethyl-, trimethyl-, and 1,1-dimethylethylenehalonium ions based on chemical shift data and long-range coupling. Our preparation of the ethylene- and propyleneiodonium and -bromonium ions now constitutes further compelling evidence for the cyclic nature of these ions and, in turn, adds force to our previous arguments. This follows from the fact that no primary or secondary alkylcarbonium ions have yet been found to be stable in antimony pentafluoride–sulfur dioxide solution (although the isopropyl cation was observed in neat antimony pentafluoride) and it is quite apparent that alkylcarbonium ions bearing a β-halogen atom should be even less stable, if only an inductive effect were operative. Thus the observation of stable haloalkyl cations derived from 1,2-dihaloethanes, 1,2-dihalopropanes, and 2,3-dihalobutanes in sulfur dioxide–antimony pentafluoride solution constitutes direct evidence that a carbon atom does not bear a full positive charge in these ions. We believe the most satisfactory representation of the ions is the cyclic three-membered ring, keeping in mind that unsymmetrically substituted ions will have unsymmetric bonding. We cannot rule out, however, a strong π-complex type species as represented by X and, moreover, we suggest that in terms of experimentally measurable physical and chemical properties, there is no difference between X and the cyclic species.



X

The rearrangement of 1,2-dimethylethylenebromonium ions to the 1,1-dimethylethylenebromonium ions shows that the latter is the more thermodynamically stable species. This further illustrates the fact that the carbon atoms in these ions must have a substantial degree of electron deficiency. Again there is a continuous increase in halogen participation from Cl to Br to I, paralleling observations in solvolysis reactions.[13]

Experimental Section

Materials. 1,1-Dichloroethane and 1,2-dichloroethane were purchased from Matheson Coleman and Bell. 1,2-Dibromoethane, propylene, and *cis*- and *trans*-2-butenes were obtained (99% pure) from J. T. Baker. 1,2-Dichloropropane and 1,2-dibromopropane were obtained from Fisher Scientific. The following compounds were prepared by the literature methods: 1-bromo-2-fluoroethane,[14a] 1-iodo-2-fluoroethane,[14b] *meso*-2,3-dibromobutane,[15] *meso*-2,3-dichlorobutane,[16] *dl*-2,3-dibromobutane,[15] *dl*-2,3-dichlorobutane,[16] β-methoxyethyl chloride,[17] β-methoxyethyl bromide,[18] β-methoxyethyl iodide,[17] *erythro*-2-bromo-2-methoxybutane,[19] and *threo*-2-bromo-3-methoxybutane.[19]

Iodofluorination. These reactions were carried out according to the general procedure described by Wood, *et al.*, and Bowers, *et al.*[20,21] (see ref 2a,b). 1-Iodo-2-fluoropropane was prepared in 38% yield, *erythro*-2-iodo-3-fluorobutane in 42% yield, and *threo*-2-iodo-3-fluorobutane in 47% yield. The stereospecificity of the addition of the elements of iodine fluoride is better than 98% as determined by vpc on a Golay column coated with Carbowax 1540 (Perkin-Elmer) operated at ambient temperature (24–26°). The products were flash distilled under vacuum to prevent decomposition, and boiling points were not recorded. These materials were not analyzed because of their instability. The absence of extraneous absorptions in their nmr spectra showed they were of satisfactory purity, although the presence of impurities was obvious by vpc.

Bromofluorination. These reactions were carried out according to the general procedure described by Kent and Freeman[20,21] (see ref 2a,b). From 8.4 g (0.2 mol) of propylene then was obtained 8.5 g (0.06 mol) of 1-bromo-2-fluoropropane of bp 71–74°, a 30% yield. The analytical sample was further purified by preparative gas chromatography.

Anal. Calcd for C_3H_6BrF: C, 25.56; H, 4.29; Br, 56.68; F, 13.47. Found: C, 25.48; H, 4.51; Br, 56.43; F, 13.60.

erythro-**2-Bromo-3-fluorobutane,**[22] bp 40–44° (67 mm), was prepared in 45% yield and *threo*-2-bromo-3-fluorobutane,[22] bp 48–51° (67 mm), was prepared in 51% yield. The stereospecificity of the addition of the elements of bromine fluoride was nearly 100% under these conditions. Only traces of the isomeric products were found by capillary vpc on a Carbowax 1540 column. (Injection of sufficient sample to activate the disk integrator on the small peak overloaded the column and gave inadequate resolution.)

Chlorofluorination. These reactions were carried out by procedures described in ref 2a and b, substituting N-chlorosuccinimide (Aldrich) for *t*-butyl hypochlorite. *erythro*-2-Chloro-3-fluorobutane,[22] bp 68–70°, was prepared in 25% yield, and *threo*-2-chloro-3-fluorobutane,[22] bp 72–73°, was prepared in 21% yield. The major products from these reactions were *erythro*- and *threo*-2-chloro-3-N-succinimidylbutanes as determined by nmr and ir; nmr in CCl_4 of the *erythro* isomers (δ in parts per million from internal TMS): −1.34 (d), J_{H-H} = 6.0 Hz; 1.48 (d), J_{H-H} = 6.5 Hz; 2.67 (s), *ca.* 4.2 (m), and *ca.* 4.4 (m); ir (neat) carbonyl at 1690 and 1765 sh cm⁻¹; *threo* isomer in CCl_4 (δ in parts per million from internal TMS): 1.40 (d), J_{H-H} = 7.0 Hz; 1.59 (d), J_{H-H} = 6.5 Hz; 2.65 (s), *ca.* 4.2 (m), and *ca.* 4.6 (m); ir (neat) carbonyl at 1710 and 1780 sh cm⁻¹.

1-Bromo-2-methoxypropane[23] was prepared by the bromination of propene in methanol at −78°. The crude reaction product was then treated with excess sodium iodide in acetone at reflux for 15 min. This procedure left some dibromide. Pure material was obtained by preparative vpc. This same reaction produced a small amount of 2-bromo-1-methoxypropane; nmr in CCl_4 (δ in parts per million from internal TMS): 1.67 (d), J_{H-H} = 6.5 Hz; 3.33 (s), *ca.* 3.5 (m), and 4.05 (m).

threo- **and** *erythro*-**2-Iodo-3-methoxybutanes.** From 2.5 ml (about 0.03 mol) of *trans*-2-butene and 5.6 g (0.025 mol) of N-iodosuccinimide in 30 ml of methanol containing five drops of concentrated sulfuric acid, there was obtained 2.6 g, 51% yield, of the desired product. From *cis*-2-butene in the same proportions there was obtained 2.4 g, 47% yield, of *threo*-2-iodo-3-methoxybutane. These compounds were purified by flash distillation. They could be passed through the capillary column at 50° without decomposition (Carbowax).

Preparation of Ions, Their Methanolysis, and Nmr Investigation. Solutions of the ions were obtained in the following way. A saturated solution of antimony pentafluoride in sulfur dioxide was prepared (at −10°). Portions (2 ml) of this solution were cooled to −78°, causing some antimony pentafluoride to crystallize from solution. To this suspension was added dropwise with stirring approximately 0.3 g of the appropriate dihalide. Slight warming was required to complete the ionization, whereupon a homogeneous solution resulted with only slight traces of color. Ion concentrations were approximately 10%. These operations were carried out in the laboratory atmosphere. When alcohols or their methyl ethers were used as precursors the same procedure was used with a solution of FSO_3H-SbF_5 (1:1) in sulfur dioxide as the acidic solvent. Spectra were recorded on a Varian Model A56-60A spectrometer with external TMS in deuteriochloroform as reference.[24]

Methanolysis of ions was accomplished by adding slowly the solution of the carbonium ion in sulfur dioxide to a suspension of methanol and potassium carbonate at −78°. Product isolation was accomplished by drowning the resulting suspension in water and extracting with pentane. Pentane was removed on a rotary evaporator and, in all cases except the chloro-*t*-butyl, cation gave a pure product (by nmr) requiring no further purification. Yields of the methanolysis products were determined by adding known

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(13) C. A. Clark and D. L. H. Williams, *J. Chem. Soc., B*, 1126 (1966); see also references contained in ref 2a and 2b.

(14) (a) B. C. Saunders, G. J. Stacey, and I. G. E. Wilding, *J. Chem. Soc.*, 773 (1949); (b) J. Hine and R. G. Shirardelli, *J. Org. Chem.*, **23**, 1550 (1958).

(15) F. G. Bardwell and P. S. Landis, *J. Am. Chem. Soc.*, **79**, 1593 (1957).

(16) H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941).

(17) L. W. Jones and D. H. Powers, *ibid.*, **46**, 2517 (1924).

(18) R. O. Roblin, Jr., J. O. Lamper, J. P. English, Q. P. Cole, and J. R. Vaughan, Jr., *ibid.*, **67**, 290 (1945).

(19) S. Winstein and R. D. Henderson, *ibid.*, **65**, 2196 (1943). We used the modification of H. O. House and R. S. Ro, *ibid.*, **80**, 182 (1958).

(20) K. R. Wood, P. W. Kent, and D. Fisher, *J. Chem. Soc.*, 912 (1966).

(21) A. Bowers, L. C. Ibáñaz, E. Denot, and R. Becerra, *J. Am. Chem. Soc.*, **82**, 4001 (1960).

(22) P. S. Fredericks and J. M. Tedder, *J. Chem. Soc.*, 3520 (1961), have prepared these compounds but did not report their boiling points.

(23) D. Gagniare, *Compt. Rend.*, **245**, 1732 (1957).

(24) We record the position of TMS in deuteriochloroform before and after the spectrum of the ion. In some previous work this was called "external TMS in deuteriochloroform." We have added 0.5 ppm to these shifts to make them relative to internal TMS in sulfur dioxide. Subtracting 0.25 ppm from our tabulated shifts changes the reference to external TMS (capillary).

Table III. Nmr Spectral Data of 1,2-Dimethylethylenehalonium Ions, Precursors, and Methanolysis Products[h]

	δ, ppm				
Compound	Compd in CCl$_4$[a,e]	Ion in SbF$_5$–SO$_2$[a,f]	Methanolysis product in CCl$_4$[a,b,e]	φ, ppm in CCl$_4$[a,g]	Δδ CHC(CH$_3$)
erythro-dl-	1.40 (d) $J_{\mathrm{H-H}} = 6.0$	1.63 (t)[c] $J = 5.0$	Complex[d]	+174.8 (d) $J = 46.5$	
$CH_3CHClCHFCH_3$	(d) $J_{\mathrm{H-F}} = 23.5$	4.02 (t) $J = 5.0$		(q) $J = 23.5$	
		4.43 (m)		(d) $J = 9.7$	
	1.52 (d) $J_{\mathrm{H-H}} = 6.0$	4.18 (t)[c] $J = 5.0$		(q) $J = 1.2$	
	(d) $J_{\mathrm{H-F}} = 1.2$	6.20 (septet)			
		$J = 5.0$			
	3.92 (quintet)				
	$J_{\mathrm{H-H}} = 6.0$				
	(d) $J_{\mathrm{H-F}} = 9.7$				
	4.44 (quintet)				
	$J_{\mathrm{H-H}} = 6.0$				
	(d) $J_{\mathrm{H-F}} = 46.5$				
threo-dl-	1.37 (d) $J_{\mathrm{H-F}} = 23.2$	1.63 (t)[c] $J = 5.0$	Complex[d]	+178.6 (d) $J = 46.4$	
$CH_3CHClCHFCH_3$	(d) $J_{\mathrm{H-H}} = 6.2$	4.02 (t) $J = 5.0$		(q) $J = 23.2$	
		4.43 (m)			
	1.51 (d) $J_{\mathrm{H-F}} = 0.7$	4.18 (t)[c] $J = 5.0$		(d) $J = 16.0$	
	(d) $J_{\mathrm{H-H}} = 6.7$	6.20 (septet) $J = 5.0$			
	4.1 (m)				
	4.7 (m)				
erythro-dl-			*erythro* 1.17 (d)	+170.9 (d) $J_{\mathrm{H-F}} = 46.8$	0.92
$CH_3CHBrCHFCH_3$	1.39 (d) $J_{\mathrm{H-F}} = 23.4$	2.61 (m)[c]	1.56 (d)	(q) $J_{\mathrm{H-F}} = 23.4$	1.22
	(d) $J_{\mathrm{H-H}} = 6.0$	}AA′X$_3$X$_3$′			
	1.69 (d) $J_{\mathrm{H-H}} = 6.8$	6.72 (m)	3.28 (s) (73% of		2.6
			3.4 (m) mixture)		2.1
			4.1 (m)		
	(d) $J_{\mathrm{H-F}} = 1.4$	2.61 (m)[c]	*threo* 1.19 (d)	(d) $J_{\mathrm{H-F}} = 9.9$	0.92
		}AA′X$_3$X$_3$′			
	4.1 (m)	6.92 (m)	1.61 (d)	(d) $J_{\mathrm{H-F}} = 1.6$	1.22
	4.6 (m)		3.28 (s)		2.8
			3.4 (m)		2.31
			4.1 (m)		
threo-dl-	1.41 (d) $J_{\mathrm{H-F}} = 23.2$	2.61 (m)[c]	*erythro* 1.17 (d)		0.91
$CH_3CHBrCHFCH_3$		}AA′X$_3$X$_3$	1.56 (d)		1.20
	(d) $J_{\mathrm{H-H}} = 6.2$	6.72 (m)	3.28 (s) (70% of	+174.0 (d) $J_{\mathrm{H-F}} = 46.4$	2.8
			3.4 (m) mixture)	(q) $J_{\mathrm{H-F}} = 23.2$	2.3
			4.1 (m)		
	1.70 (d) $J_{\mathrm{H-H}} = 6.9$				
	4.1 (m) $J_{\mathrm{HF}} = 46.4$	2.61 (m)[c]	*threo* 1.19 (d)	(d) $J_{\mathrm{H-F}} = 16.6$	1.61
		}AA′X$_3$X$_3$′	1.61 (d)		
	4.6 (m)	6.92 (m)	3.28 (s)		1.20
			3.4 (m)		2.8
			4.1 (m)		2.1
erythro-dl-	1.46 (d) $J_{\mathrm{H-F}} = 23.6$	3.07 (m)[c]	1.17 (d) $J_{\mathrm{H-H}} = 6.0$		1.61
$CH_3CHICHFCH_3$		}AA′X$_3$X$_3$′			
	(d) $J_{\mathrm{H-H}} = 6.0$	6.87 (m)	1.82 (d) $J_{\mathrm{H-H}} = 6.0$	+165.7 $J_{\mathrm{H-F}} = 47.0$	1.20
	1.87 (d) $J_{\mathrm{H-H}} = 6.9$		2.9 (m)		
	(d) $J_{\mathrm{H-F}} = 1.0$		3.28 (s) (76%)	$J_{\mathrm{H-F}} = 23.6$	2.8
	4.05 (m) $J_{\mathrm{HF}} = 47.0$		4.2 (m)	$J_{\mathrm{H-F}} = 10.6$	2.1
	4.7 (m)			$J_{\mathrm{H-F}} = 1.0$	
threo-dl-	1.39 (d) $J_{\mathrm{H-F}} = 23.5$	3.07 (m)[c]	1.20 (d) $J_{\mathrm{H-H}} = 6.5$		1.68
$CH_3CHICHFCH_3$		}AA′X$_3$X$_3$′		+167.1	
	(d) $J_{\mathrm{H-H}} = 6.1$	7.14 (m)	1.78 (d) $J_{\mathrm{H-H}} = 7.0$		1.20
	1.87 (d) $J_{\mathrm{H-H}} = 6.9$		3.2 (m)	$J_{\mathrm{H-F}} = 47.0$	3.1
	4.0 (m) $J_{\mathrm{HF}} = 47.0$		3.28 (s) (78%)	$J_{\mathrm{H-F}} = 23.5$	2.4
	4.7 (m)		4.2 (m)	$J_{\mathrm{H-F}} = 19.0$	

[a] Abbreviations used are: s = singlet, d = doublet, q = quartet, t = triplet, m = multiplet. [b] Figures in parentheses are isolated yields. [c] See text for structural assignments. [d] Chloro-*t*-butyl methyl ether was detected by vpc; see also ref 2a. [e] Internal TMS. [f] External TMS. [g] Internal CFCl$_3$. [h] *J* values in hertz.

weights of material to the antimony pentafluoride–sulfur dioxide solution and represent the over-all yield of the ionization and solvolysis reactions. Identification of products was made by glpc comparison of retention times with authentic samples and by nmr and ir spectroscopy.

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